Approaches for Downgradient Reactive Transport Modeling at Uranium In Situ Recovery Sites

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Office of Legacy Management

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Funding Sources and Collaboration

- U.S. Department of Energy Office of Legacy Management
- U.S. Environmental Protection Agency
- U.S. Geological Survey (USGS)
- Collaboration with the South Dakota School of Mines and Technology, Rapid City, South Dakota
- Collaboration with the University of Witwatersrand, Johannesburg, South Africa
- Core provided by Powertech (USA) Inc.

Outline

- Objectives
- Dewey Burdock site
- Sorption and batch testing
- Reactive transport modeling
- Data needs to reduce uncertainty
- How-to procedures
- Conclusions

Objectives

Reactive transport modeling downgradient from a future uranium in situ-recovery zone for a better understanding of groundwater quality protection

- Use state-of-the-art modeling procedures
    - Latest modeling codes and updated databases
- Evaluate uncertainties
- Provide a consistent procedure for future applications

Goal from limited samples is to provide a better understanding of the mechanisms, and get a feeling for uncertainties to guide future data collection and provide a good methodology to follow.
The objective is NOT a precise prediction.
Model codes continue to be updated, key state-of-the-art for this work is going beyond the Kd, retardation approach, and doing full reactive transport modeling.

Dewey Burdock

- Proposed uranium in situ-recovery site in the southwest corner of South Dakota
- Focus on oxidized side of the uranium ore (more risk of uranium mobility and test uranium sorption to iron hydroxides)
- Measured solid-phase iron and did sorption batch tests – USGS

MONTANA

SOUTH DAKOTA

WYOMING

Black Hills

Study Area

NEBRASKA
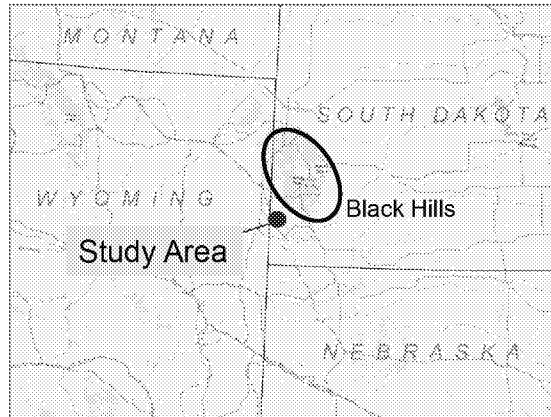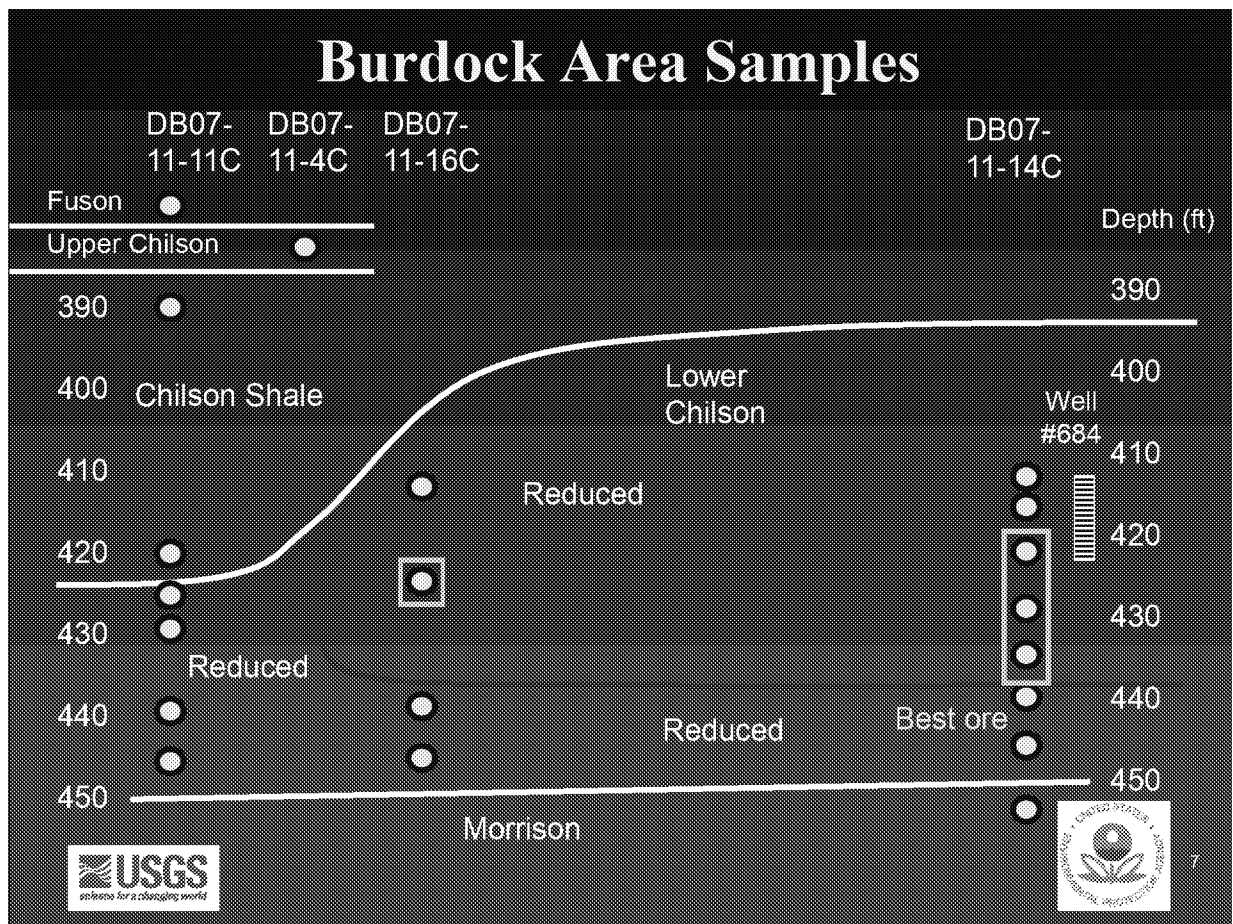
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In terms of uranium mobility, sorption of uranium on iron hydroxides is generally less than sorption to organic carbon (reduced side).
Next slide has more details on oxidized vs. reduced distribution.
Current research at the South Dakota School of Mines is using reduced side core.

Oxidized Zone

Proxy core locations

Modified from Powertech and Frank Lichnovsky

Black dots are exploration holes and, in general, represent the ore zones.

Current groundwater flow is NE to SW, but groundwater during ore formation was likely NW to SE, which provides the setting for the oxidized zone to be downgradient.

With current groundwater flow direction, groundwater will eventually cross the oxidized zone into the surrounding reducing zone. However, groundwater will cross the aquifer exemption boundary (main compliance point) within the white/yellow rectangle.

No directly downgradient oxidized core is available; needed to use "proxy" core that was collected during exploration drilling (next slide).

Burdock Area Samples

Sample locations and additional solid phase data are part of USGS Open-File Report 2013-1093.
Samples for this talk are focused on the oxidized lobe within the ore zone.
Well #684 was used for background groundwater quality; no really good background well in the zone being evaluated.
Green boxes indicate sample locations.
ID for sample points are sequentially numbered with depth.
Using old slide format, as this is from a USGS report/representation, with EPA funding.

Question: Post-Restoration Risk of Downgradient Transport if Uranium Is Left?

- Future risk exists, so predictive modeling is required, with reasonable assumptions
- No "plume," so how do we calibrate a model?
- Downgradient rock/water interactions are needed
- Use solid-phase iron concentrations, sorption batch tests, and groundwater quality
- Can adequate predictions be made with just the knowledge of solid-phase iron concentrations or do we need to use sorption batch test data?

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Initial goal is for restoration to pre-mining conditions, but historically uranium ACLs have been necessary (Wyoming and Texas). Focus for this talk is on uranium, but other elements could be important, like radium.

Sorption Processes

- Constituents in solution (UO_2^{2+}, uranyl ion, plus signs) are attracted to a charged surface (bar with minus signs)
- Surface charge can change with the groundwater geochemistry (e.g., pH)
- Constituent "availability" for a sorption reaction can change with the groundwater geochemistry (uranyl ion likes to complex with carbonates)

More carbonates

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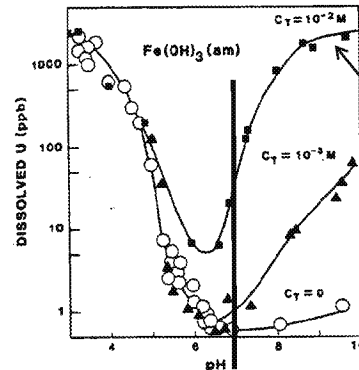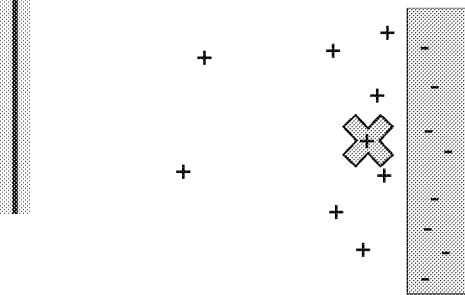
Hsi and Langmuir, 1985

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Review on sorption processes.
The bar with the minus signs represent the charged surface and the plus signs represent the constituents. The animated X over the plus sign is to indicate that this constituent is not "available" for sorption.
Diagram is very important to remember, that pH and amount of carbonates have a strong influence on sorption.
Note large slope in sorption change at pH 7 and higher carbonate content for future reference (animated line).

Batch Tests and Iron Measurements

- Test sorption capacity with a sorption "isotherm"
- Beaker of solid-phase material in contact with lab-prepared "groundwater," spiked with three different uranium concentrations
- Separately measured solid-phase iron content (total and with sequential extractions)
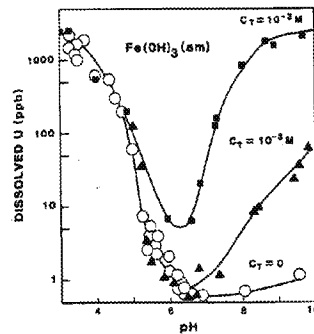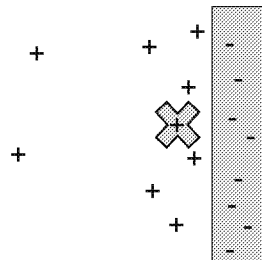
Uranium in solution

Solid sample with sorbed uranium
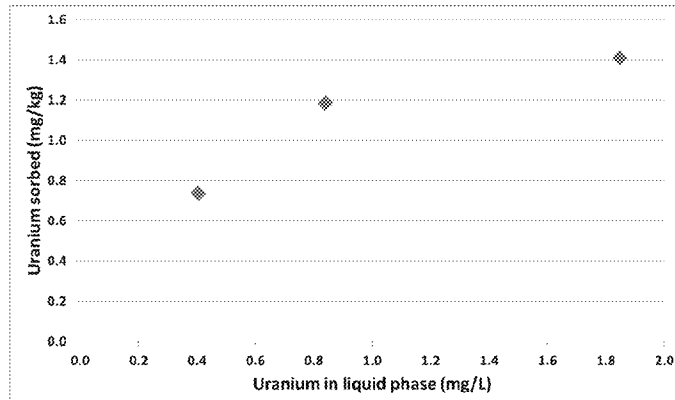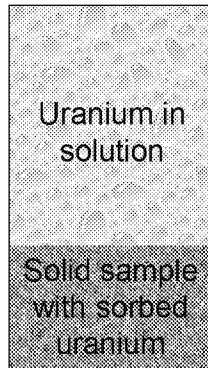
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Term isotherm refers to a test at a constant temperature. But overall, a test at one geochemical condition.
Point out that first spike was about 0.6 mg/L, then plot final concentration in liquid, amount on solid is the uranium lost from solution. Plot is final equilibrium sorption. Similar routine for other concentrations.
Iron measurements with sequential extractions, because amorphous Fe oxyhydroxides generally provide a stronger sorption capacity.

Geochemical Modeling Via PHREEQC for Simulated Sorption on Iron

- Program uses full suite of geochemical data to determine the amount of "free ions" available for sorption
- If a database is available, PHREEQC can calculate the sorption capacity of the solid phase
- PHREEQC has the Dzombak and Morel, 1990 database for sorption on **iron hydroxides** with multiple cations

Hsi and Langmuir, 1985
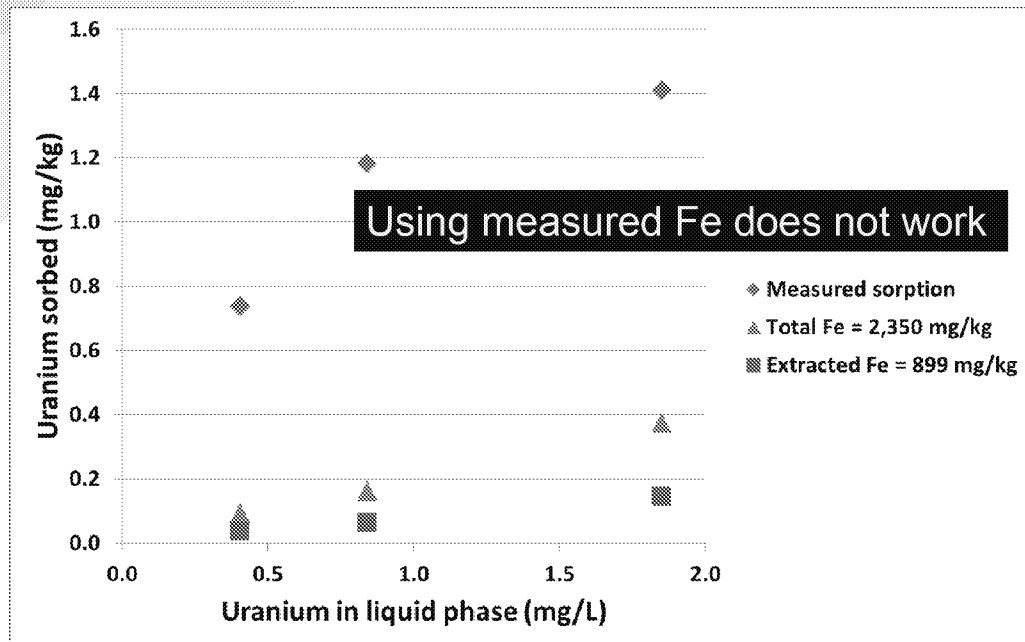
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Attractive to try iron oxyhydroxide sorption first, since that database is available.

Measured Sorption Compared to Predicted Sorption with Measured Iron Concentrations

Data is from sample 11-14C-4.
Not a total surprise, since 1990, researchers have gone to component additive models and generic sorption.

What Is the Sorbent?

- Iron?
- Clays?
- Organic carbon?
- A generic sorbent is needed
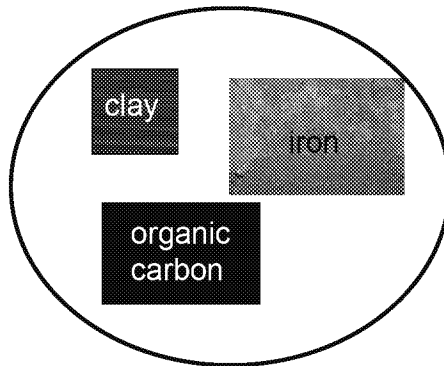
Generalized Composite Surface Complexation Approach

- Follow procedures used by Jim Davis, Gary Curtis, and others at the Naturita, Colorado, uranium-mill-tailings site
- Independent of the specific sorbent material
- Use the latest database for uranium complexation
- Create a calibrated generic sorption model of the batch sorption tests using PHREEQC and PEST (automated calibration routine)
- PEST adjusts the sorption parameters (equilibrium constants and sorption site densities) to get the best fit to the measured data

Naturita is a DOE LM site in western Colorado where uranium transport in groundwater after tailings were removed was the issue. Series of published papers.
New uranium complexation data by NEA and Dong and Brooks, 2006.
Details on this slide could be a whole separate technical talk, will focus just on the results.

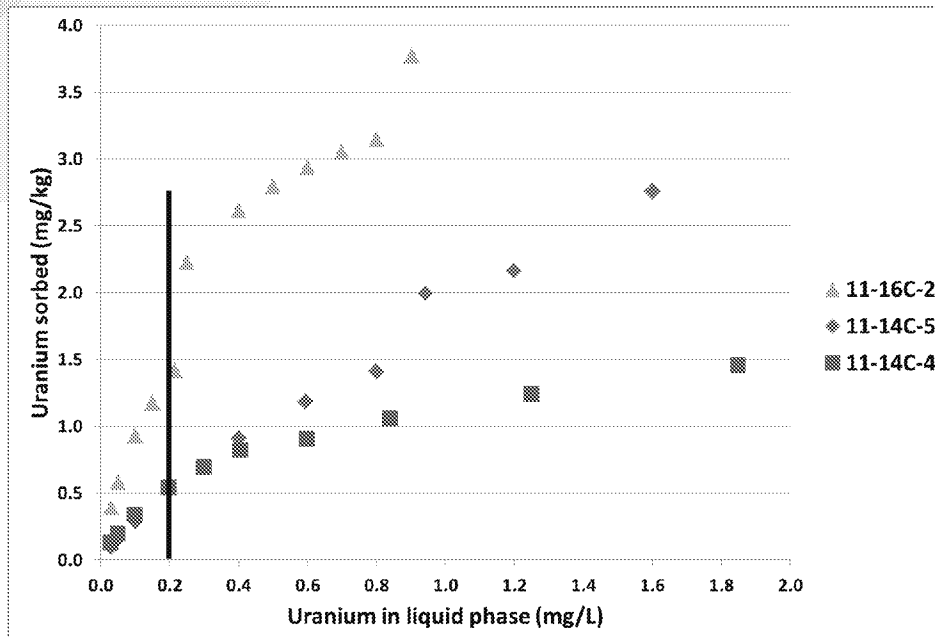# Generalized Composite Surface Complexation Calibration: Best Fit
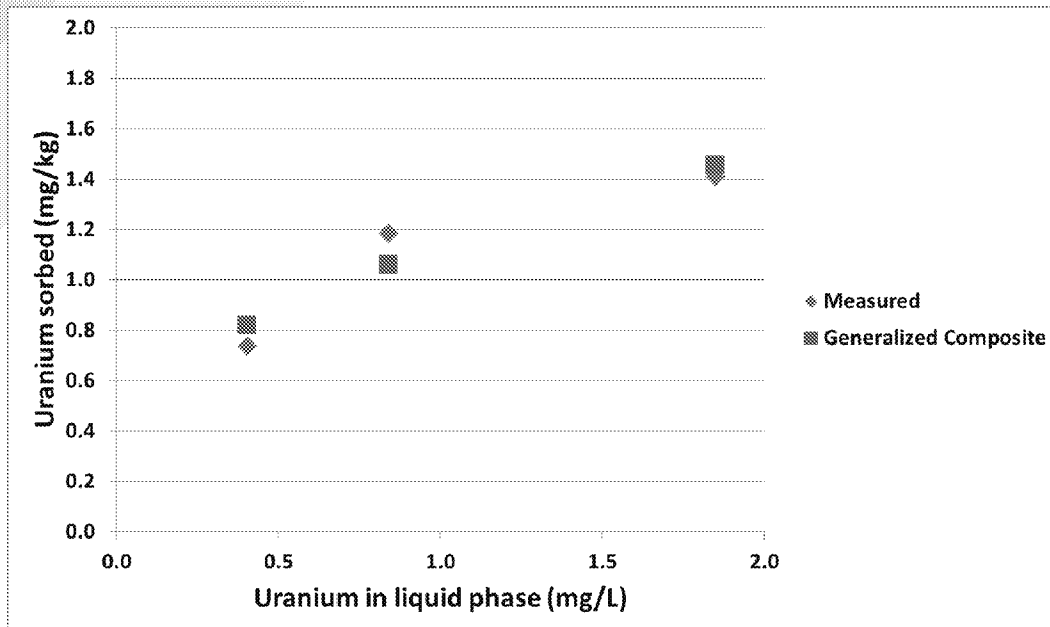
This fit provides the final sorption parameters used in the reactive transport models.

Fourth sample was not used because of high vanadium – possible mineral precipitation.
This slide is the final, best fit calibration sorption curves for all three samples. Note the "jumps" in the curves are due to slightly different final batch waters at the three uranium concentrations (hint that slight changes in geochemistry are important).
Note that 11-14C-4 and 11-14C-5 have similar sorption up to about 0.4 mg/L of uranium, but sorption curves are different at higher uranium concentrations. Thus, any predictions with sorption may be different depending on the uranium concentration used.
11-16C-2 has an overall higher sorption capacity (also the highest iron content).
All of the predictions use the parameters that were used to create these sorption curves.

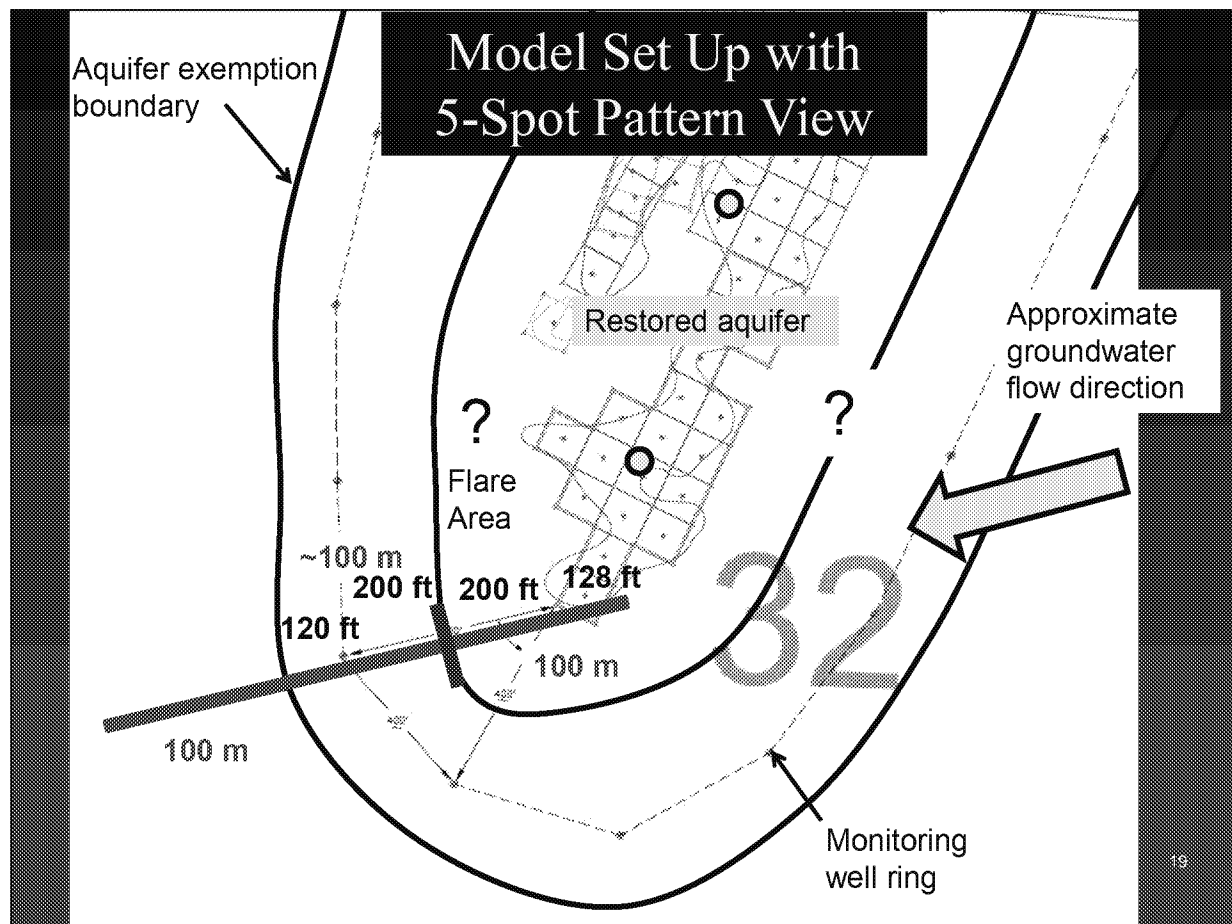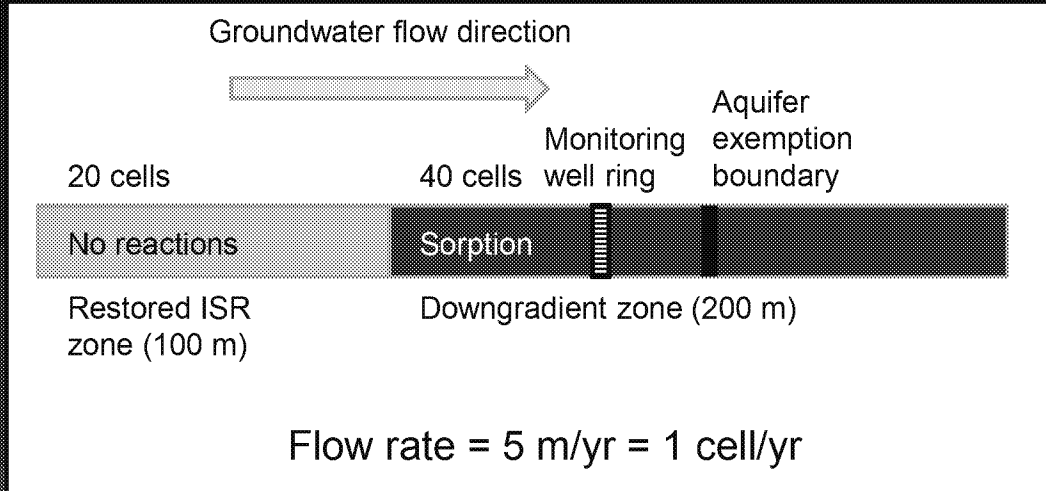# Finally Ready to Do Some Predictions

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Sorption calibration is a critical first step that takes significant time and effort.
Running the predictions is the easiest part, since the "calibration" data has already been provided (batch tests), unlike an existing groundwater plume.
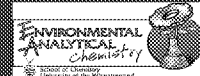
Conceptual View of the Modeled Zone

Again, focus is on the oxidized side, but the procedures are directly applicable to sorption on the reduced side (might also need to account for precipitation).
This geometry is unique to Dewey Burdock. Easy to change for a different site.
Used old slide format, as this is from a USGS report/representation.

Model Set Up with 5-Spot Pattern View

Animated red line indicates the end of the restored zone and essentially the starting point for downgradient sorption reactions.
Would be easy enough to adjust specific geometry for different sites.
EPA regulations require no impact on groundwater quality beyond the aquifer exemption boundary (with a 20% leeway for analytical error).
Used old slide format, as this is from a USGS report/representation.

Model Set Up

Groundwater flow direction

Monitoring Aquifer
well ring exemption
boundary

20 cells   40 cells

No reactions   Sorption

Restored ISR   Downgradient zone (200 m)
zone (100 m)

Flow rate = 5 m/yr = 1 cell/yr

One-dimensional reactive
transport with PHREEQC

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ANALYTICAL
Chemistry
School of Chemistry
University of the Witwatersrand

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Flipped around so flow is left to right and matches graphs (hard to draw right to left).
Restored ISR zone ends at the end of the flare area; assumed to be 200 ft. from the nearest injection well (flare area is not actually known at this point).
Mention that left side always has incoming, background groundwater, and assumption is no reactions in the restored ISR zone.
Again, dimensions and flow rate are easily adjusted for site specifics.
Used old slide format, as this is from a USGS report/representation, with University of Witwatersrand collaboration.

Prediction Range with Uncertainties

- Models all use 0.2 mg/L uranium; results are for sample 11-14C-4 unless otherwise noted
- Based on sample heterogeneity
  - Best calibrated and 11-16C-2 with more sorption
- Based on reaction assumptions
  - Use calcite equilibrium (and 11-16C-2)
- Based on groundwater measurement from well #684
  - Increase pH by 5 percent
  - Decrease pH by 5 percent
- Based on possible restoration and groundwater measurement
  - pH of 6 in restored zone and 5 percent increase in pH for background

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Indicate that 11-14C-4 and 11-14C-5 give similar prediction results with 200 ppb uranium, so only 11-14C-4 is presented. Would get different results at higher U concentrations.
11-16C-2 has the higher sorption capacity, so present a separate best calibrated version for it.
All graphs will show full column at 30 years and then 300 year time series at the monitoring well ring.
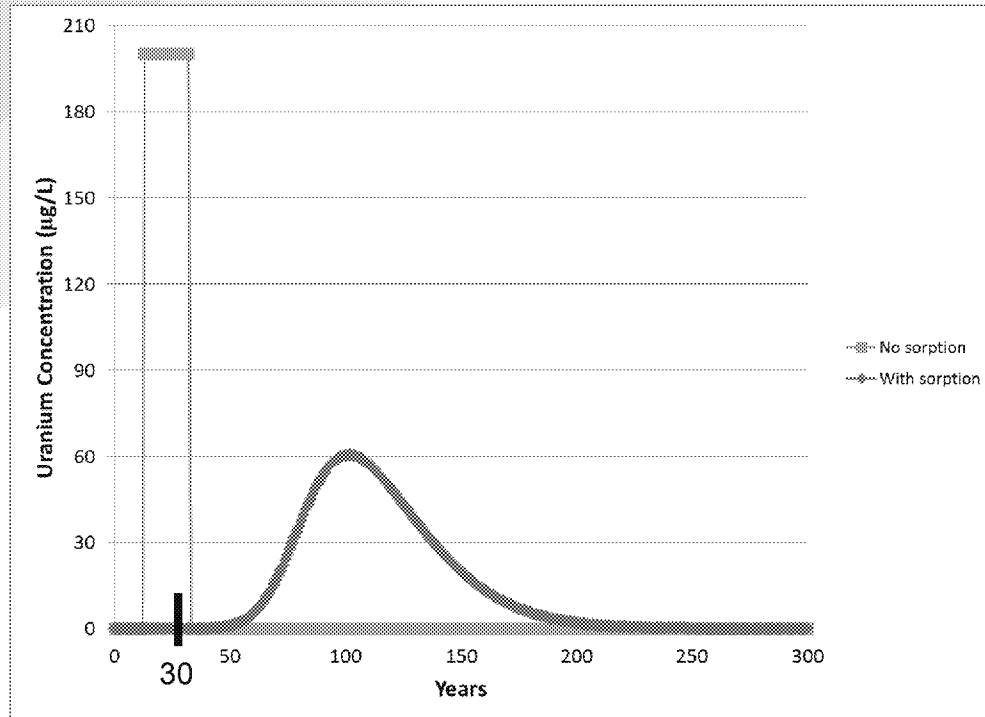
Best Calibration: 30 Years
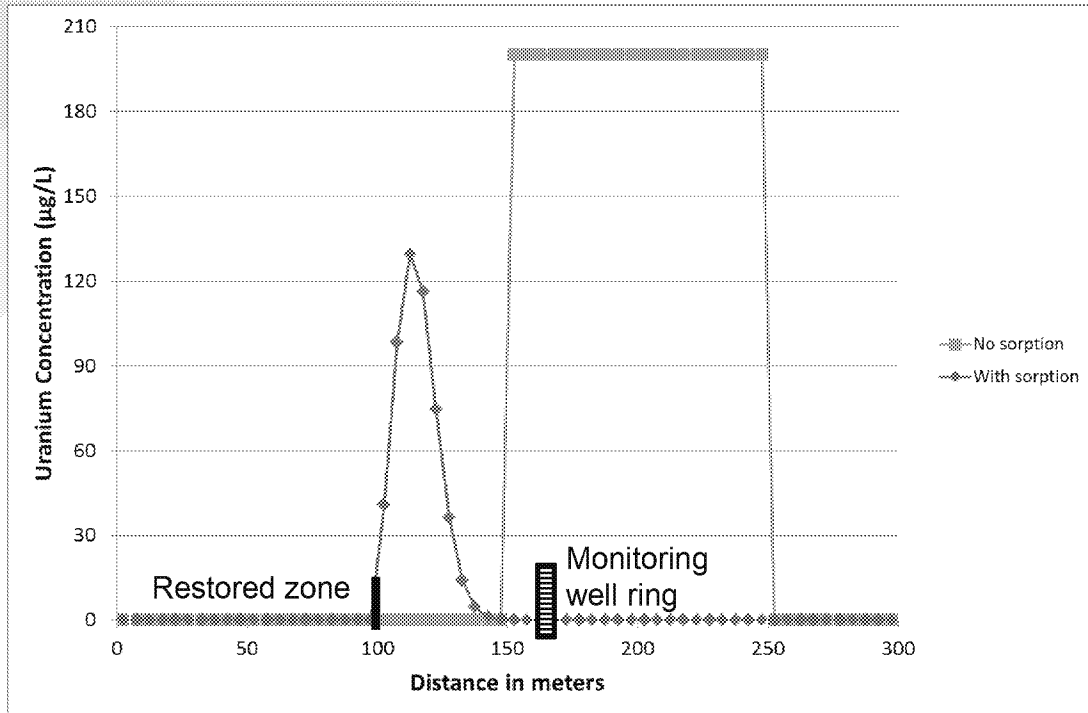
Restored zone = 100 m, downgradient zone = 200 m. Monitoring well ring is 200 feet or 62.5 meters from the end of the flare zone (400 ft. from the nearest injection well).
After 30 years the conservative water has moved 150 m and is almost past the monitoring well ring.
Well #684 water was used for the initial water throughout the column, except for the addition of 200 ppb uranium in the restored zone (seen as the no sorption curve).
For this modeling, the actual restored groundwater quality is unknown.

Best Calibration: Monitoring Well Ring

Best Calibration: 11-16C-2 at 30 Years
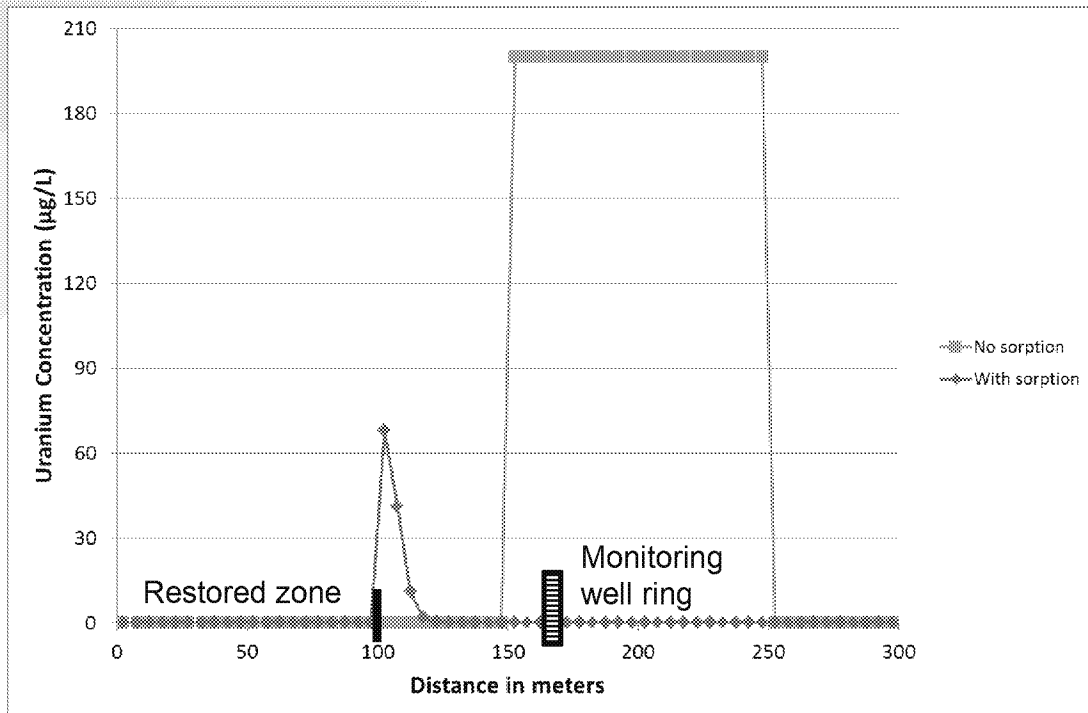
Sample with more sorption.

Best Calibration: 11-16C-2 at Monitoring Well Ring
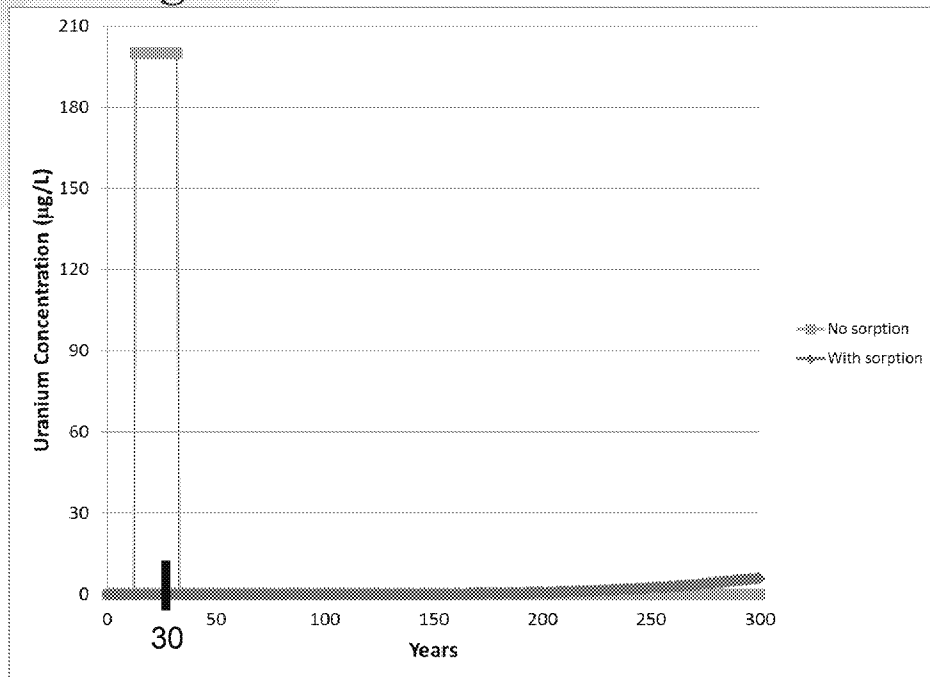
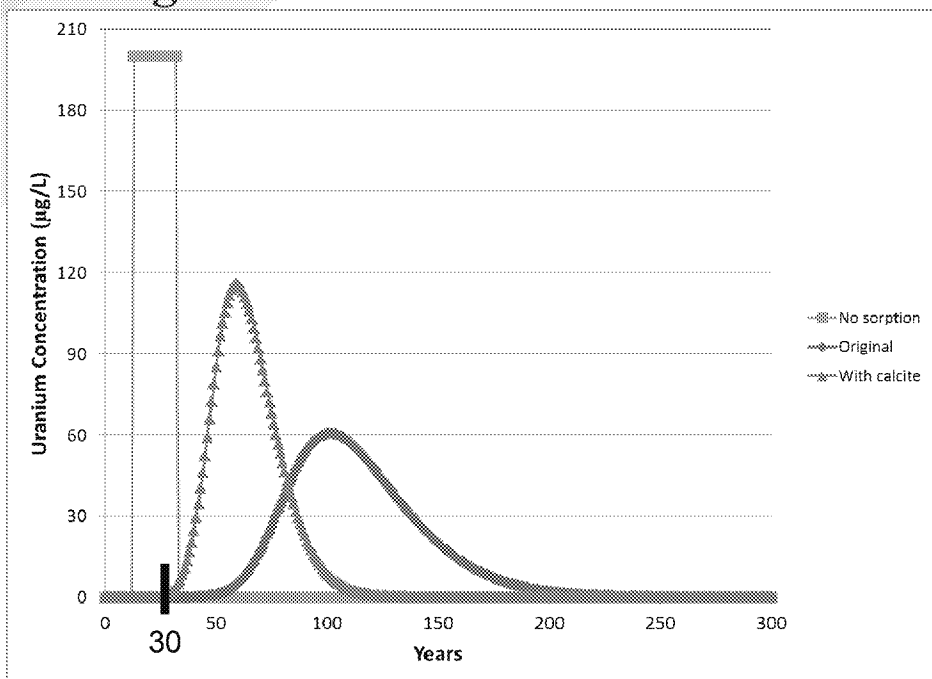# With Calcite Equilibrium at 30 Years

Initial simulations use no reactions in the restored zone, and sorption only in the downgradient zone (the blue original line, best calibration curve).

Same curve colors and symbols on all upcoming slides, blue curve is the original simulation, best calibration, with downgradient sorption only.

This simulation has calcite equilibrium applied for both zones throughout the column (green, with calcite). No sorption curve (light red) is without any reactions.

Groundwater from well #684 gives a calcite SI of -0.14 (slightly undersaturated, so this simulation will dissolve a bit of calcite). This is a pH difference of 0.14 pH units. Very high sensitivity.
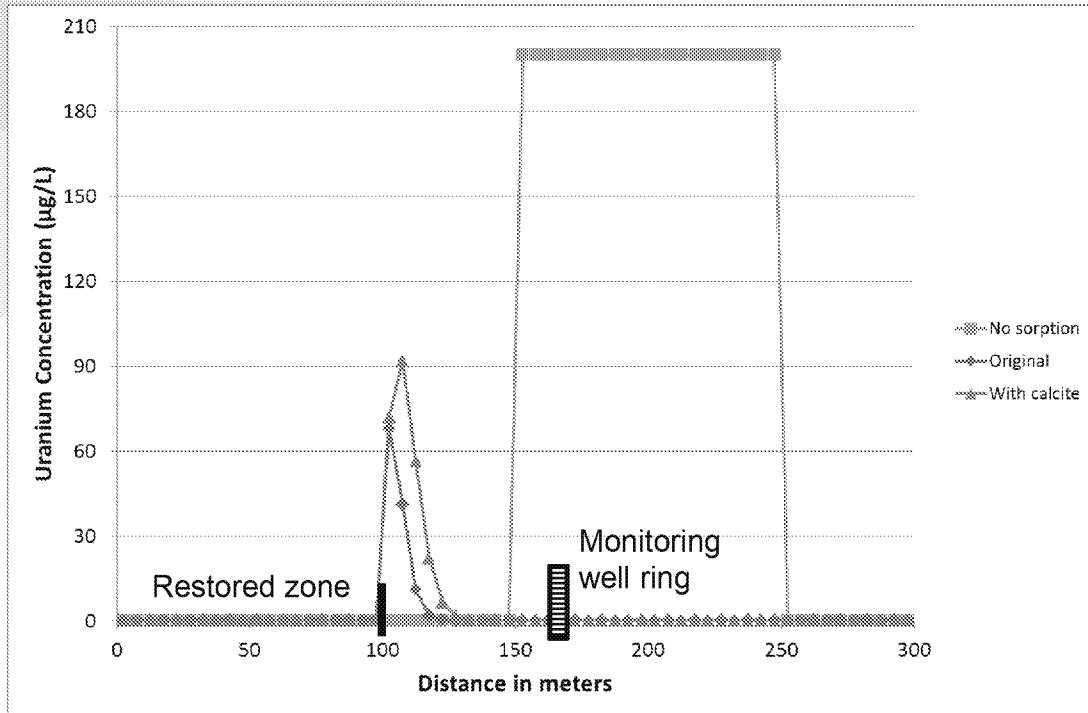
With Calcite Equilibrium at Monitoring Well Ring

11-16C-2 with Calcite Equilibrium at 30 Years

11-16C-2 with Calcite Equilibrium at Monitoring Well Ring

5 Percent Increase in pH at 30 Years

For all zones, pH was increased by 5 percent from 6.78 to 7.12. Initial pH measurement is from well #684, which is the initial water in all zones except restored zone had 200 ppb uranium added.

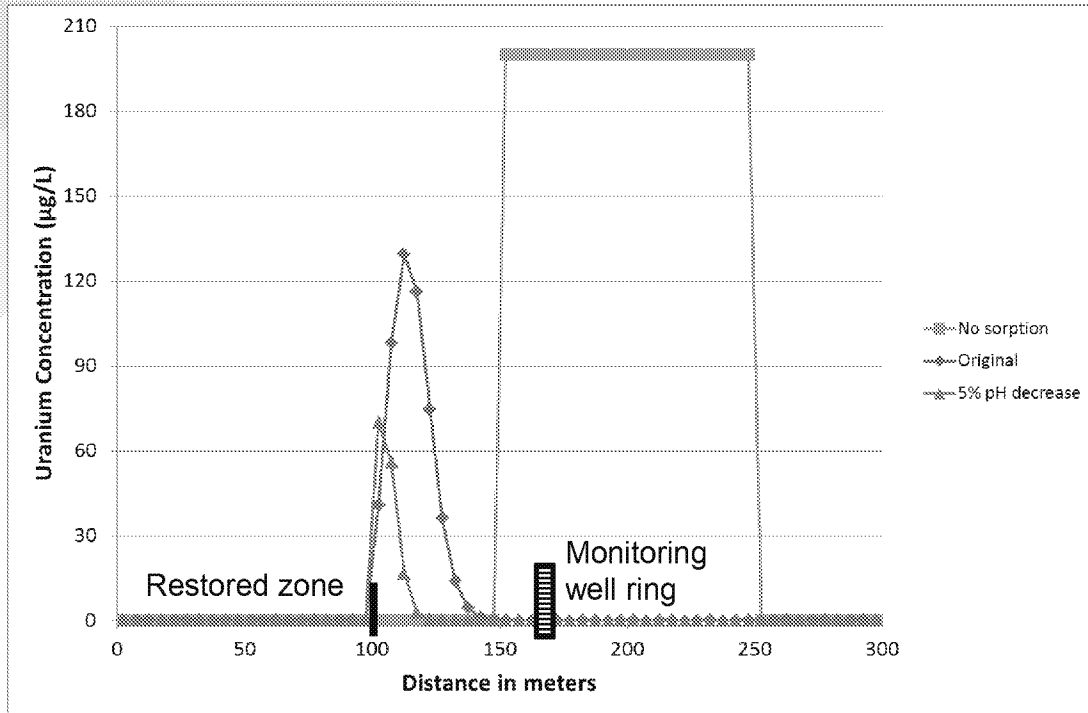# 5 Percent Increase in pH at Monitoring Well Ring
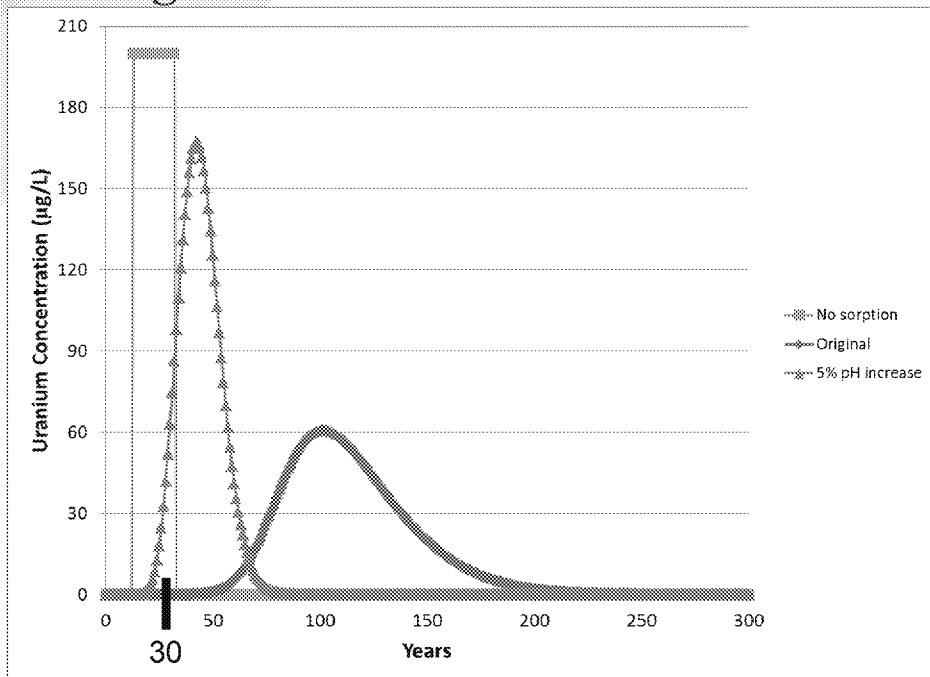
Big difference, remember steep slope on sorption curve versus pH.

5 Percent Decrease in pH at 30 Years

For all zones, pH was decreased by 5 percent from 6.78 to 6.44. Initial pH measurement is from well #684.
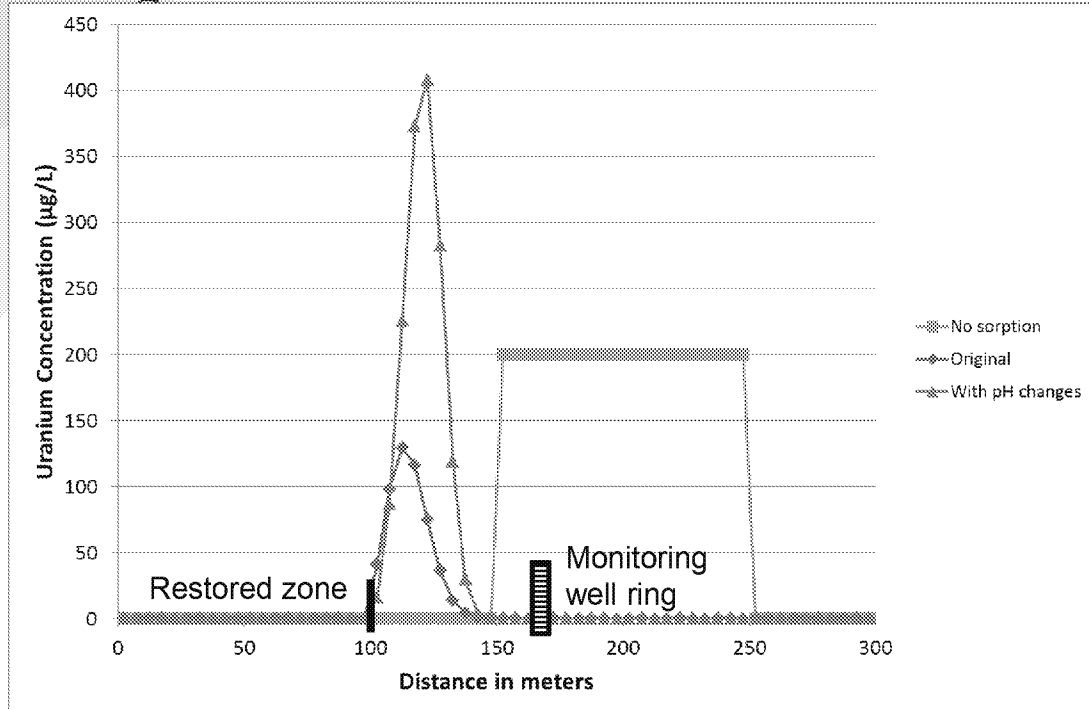
5 Percent Decrease in pH at Monitoring Well Ring
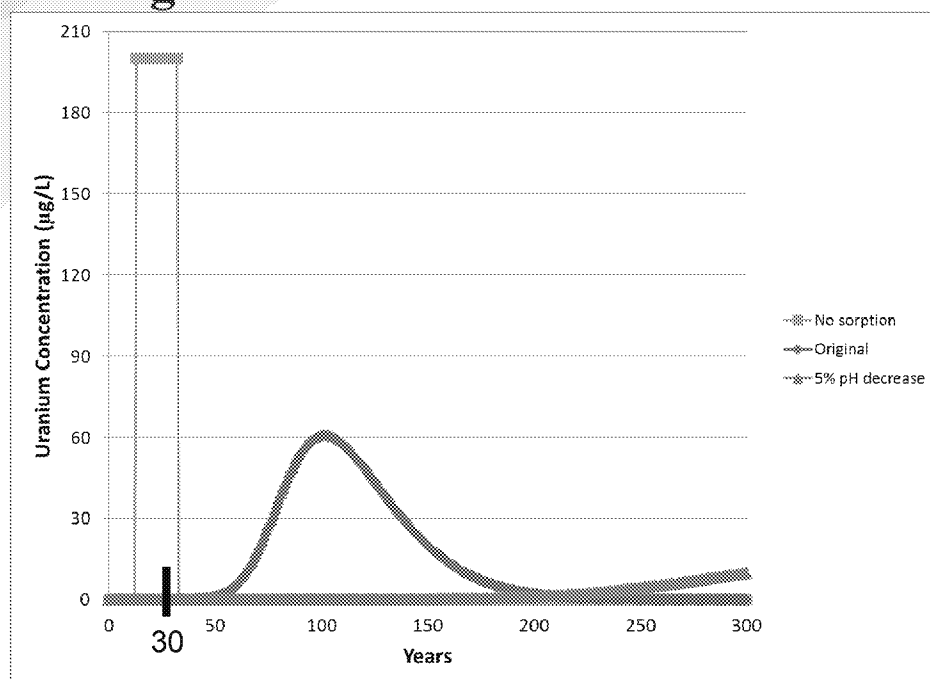
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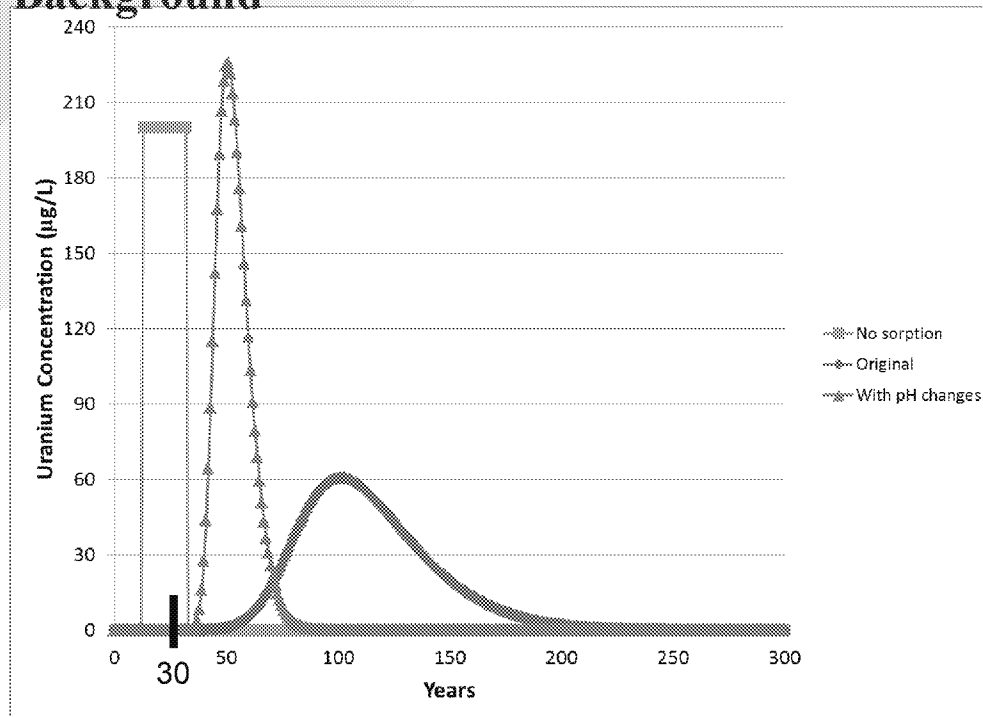pH 6 in Restored Zone, 5 Percent pH Increase in Background at 30 Years

Background is the same as well #684. No real background wells currently exist for the zone being evaluated.

pH 6 creates additional sorption of uranium that is later desorbed by the background groundwater.

Main point, have to have accurate groundwater geochemistry.

This is without calcite dissolution, which is not too realistic downgradient (test in next series of slides). However, this condition could occur in the restoration zone (or downgradient) if calcite is consumed (or did not exist prior to the ISR) and uranium is sorbed to leftover iron oxyhydroxides. So, longer term stability in the restoration zone depends on background groundwater geochemistry and the solid-phase mineralogy.

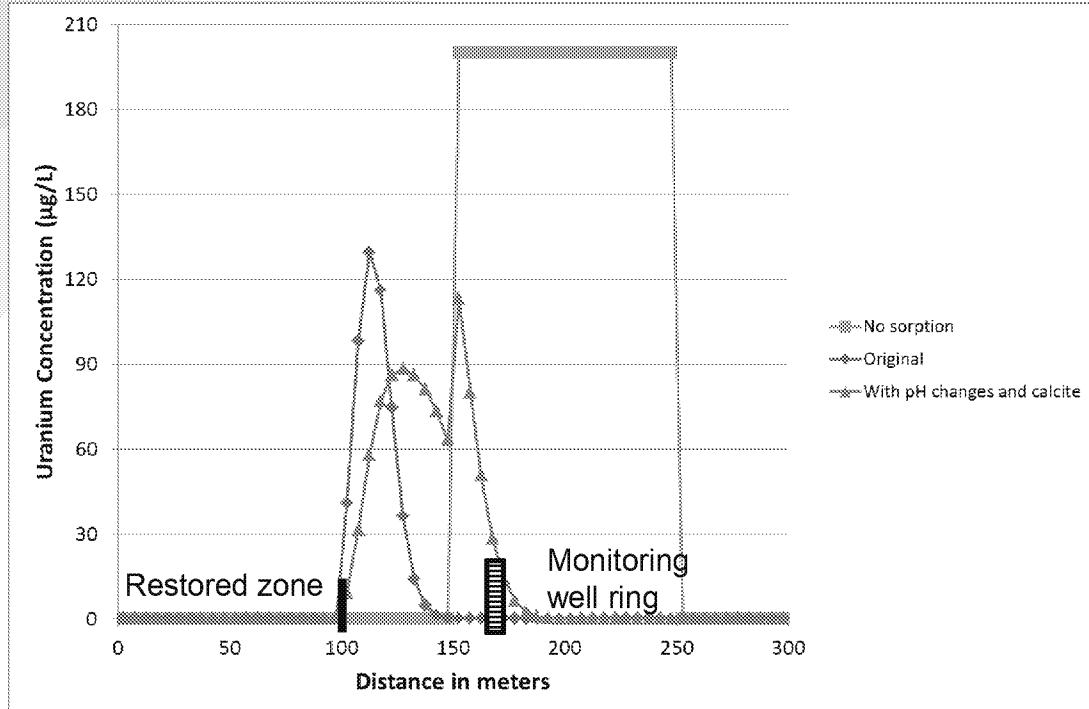# pH 6 in Restored Zone, 5 Percent pH Increase in Background

Thin zone with high uranium concentrations, at 55 years, even higher than the 200 ppb that was left behind.

pH 6 in Restored Zone, 5 Percent pH Increase in Background with Calcite at 30 Years

Put the thinking cap on!

Now with addition of measured calcite amount throughout the 1D column, allowed to come to equilibrium. The pH of 6 actually dissolves more calcite and increases the carbonate content. Thus, less sorption with pH 6 restored water and more sorption with 5 percent pH increase in background groundwater (with higher pH actually precipitates calcite, so less carbonate in solution) and then the curve "restarts."

Now similar to other simulations compared to curve with no calcite, but with interesting ups and downs due to geochemistry.

Final Range (11-16C-2 to 5 Percent pH Increase)

11-16C-2 Best Calibration at 30 Years

11-16C-2 Best Calibration at MW Ring

11-14C-4 at 30 Years, 5% increase in pH

11-14C-4, 5% increase in pH, at MW Ring

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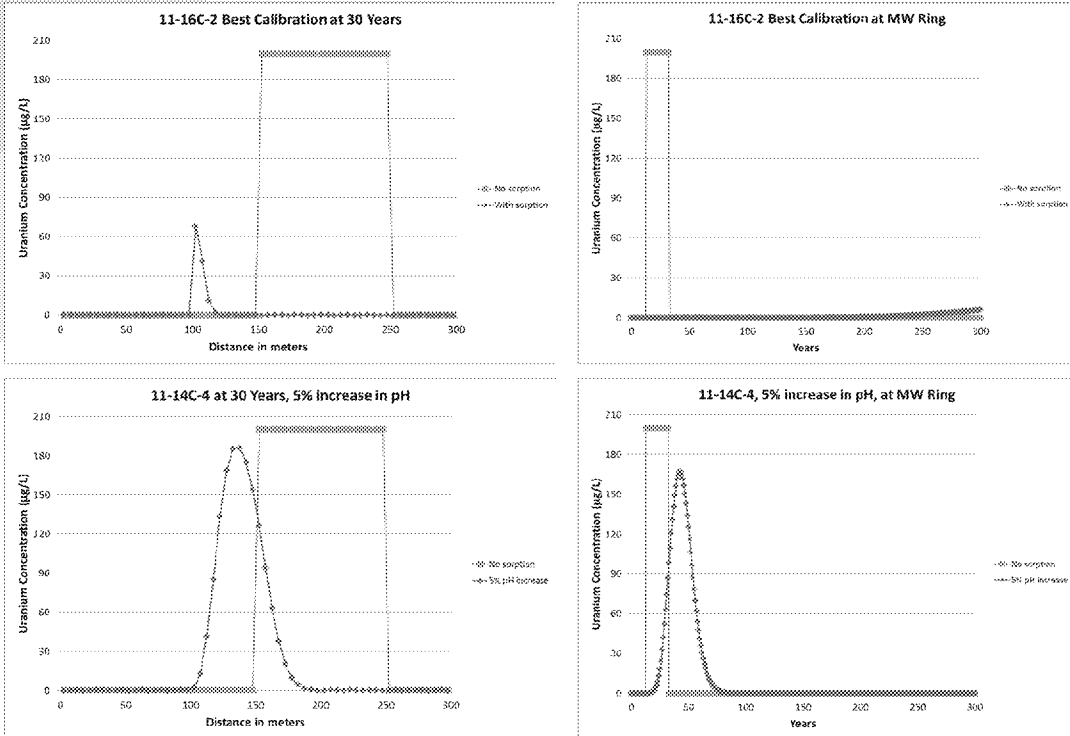
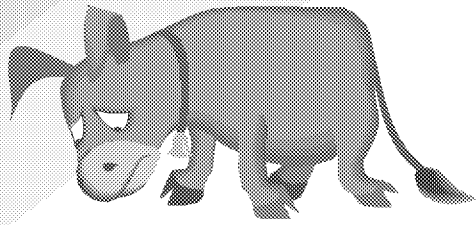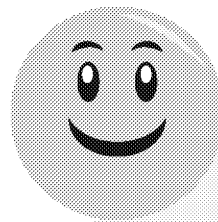5 percent pH decrease is a close second to 11-16C-2, but this is the overall maximum reasonable range.

Big Prediction Range!

BUT, did learn some important things about how the system works

Good part is this effort was not meant to provide a final prediction.

Added Data to Potentially Reduce Prediction Ranges

- Actual downgradient core from multiple intervals
- Batch testing with more calibration points
  - Added uranium concentrations
  - Change pH, alkalinity, and calcium
- Column testing for 1D calibration*
  - Test different uranium concentrations
  - Test influence of pH, alkalinity, and calcium
- Pilot field studies#
- Very accurate background and post-restoration groundwater geochemistry
- Evolution of background groundwater as it flows into the restored zone

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Critical to get true downgradient core and test variability with depth. With just three samples, current range of uncertainty is highly dependent upon sample differences.

Added calibration points on batch testing will allow for better sorption parameter estimates. This was done at the Naturita site, but not at Dewey Burdock due to limited funding. This is being done for Smith Ranch-Highland work.

pH, alkalinity, and Ca changes all influence uranium mobility (mainly complexation influence).

* after column testing indicates doing this step is a good idea, but maybe not absolutely necessary. Would provide very good 1D data for model calibration.

after pilot field studies indicate this is the best ultimate best data.

Column testing is the best we can get to calibrate a 1D predictive model without a field test. Large prediction range in modeling results indicate the need for this additional calibration data. Field injections of uranium in the downgradient zone are unlikely, but uranium injections in ore zones are about to occur at Smith Ranch.

Underlined geochemistry data to emphasize large change in predictions.

Added evolution of background groundwater, as this was not evaluated, but will be a critical step in possible geochemistry changes. Analyses may not show any changes, but still critical to double check.

How-To Procedures

- Collect representative downgradient core (multiple intervals) and characterize the mineralogy
- Collect representative core in restored zone (multiple intervals) and characterize the mineralogy
- Contact restored zone core in a column with background groundwater to produce an evolved background groundwater in the restored zone
- Do batch and column testing using the downgradient core with the final restoration groundwater and the evolved background groundwater
  - Use multiple uranium concentrations and multiple geochemical conditions based on observed variations in field data
- If a reducing zone, maintain anoxic conditions and also evaluate uranium precipitation

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Procedures require post-restoration sampling and data.
Emphasize that mineralogy should be quantitative, especially for calcite.
"Evolved" groundwater could be as simple as filing up a column with background groundwater, let is sit for several days or more (to equilibrium), and then drain out the water and sample it.

How-To Procedures (continued)

- Calibrate using data from batch and column tests to determine final sorption parameters (and precipitation potential)

- Do reactive transport modeling predictions (1D/2D/3D) with final restoration waters, evolved background groundwater, and background groundwater, in series

- Evaluate prediction ranges based on analytical uncertainties, natural heterogeneity (solid and water), and calibration uncertainties

- Use modeling as a tool for restoration targets and/or justification for possible alternate concentration limits (ACLs)

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Second bullet – the contacting groundwater in the downgradient zone will be the restoration waters first, then evolved background groundwater, and then check unchanged background groundwater for very long term influence.
Final bullet – able to run reactive transport models "real time" with the restoration and evaluate whether or not continued restoration is required.

Conclusions

- For the oxidized zone at Dewey Burdock, modeling sorption with solid-phase iron concentrations is not sufficient, need to model using generic sorption
- Sorption can provide a significant natural attenuation mechanism for uranium
- Reactive transport modeling can have uncertainties that produce large prediction ranges
- Very accurate solid-phase geochemistry is critical
- Very accurate groundwater geochemistry is critical

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"Significant" cannot be quantified at this point.
On bullet three, having only three samples allows for establishing the procedures and evaluating uncertainty, certainly is not enough for a "final answer."

Conclusions (continued)

- Apply reactive transport modeling with careful consideration and review of:
    - Model assumptions (reactions, sorption representation, database, etc.)
    - Analytical errors (lab and field)
    - Calibration uncertainties (goodness of fit, non-uniqueness, etc.)
- Will always have to deal with site heterogeneity............

Which Requires Appropriate Monitoring
Use in Conjunction with Modeling

Stakeholder
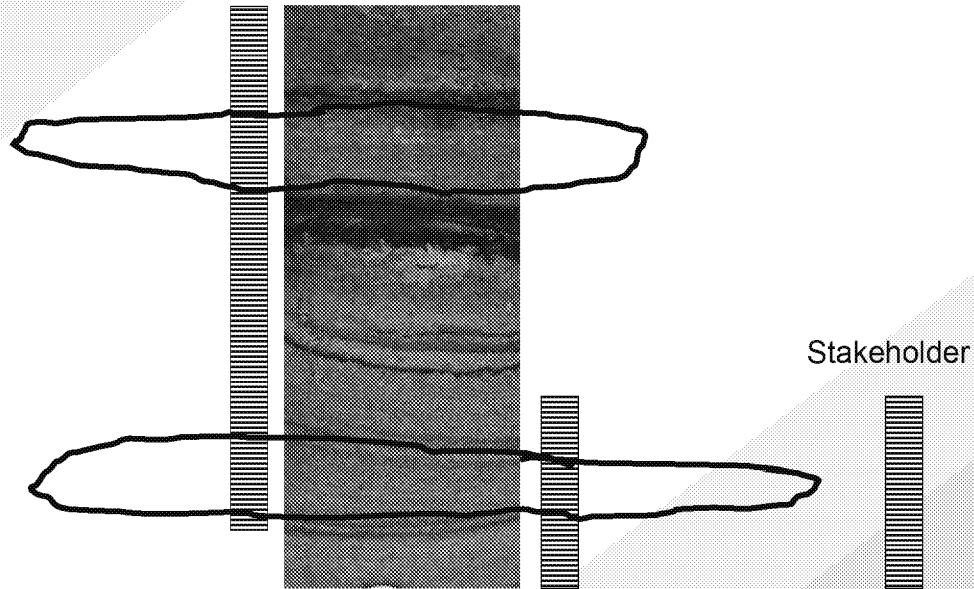
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Actual downgradient Dewey Burdock core. Oxidized with a layer of organic carbon.
Sample results will depend on well screen intervals and how any modeling deals with the lumping of heterogeneity.
Use monitoring and modeling iteratively. Modeling can help with appropriate monitoring locations and monitoring results can be fed back into the model for better predictions.

Journal Articles

1. Summarize procedures for iron measurements and batch testing. Highlight need for generic sorption beyond just Fe. Demonstrate the use of PEST with the sorption batch studies. Show calibration issues with limited data, local minimums, and correlation of parameters.

2. Final predictions with large uncertainties. List additional data needs to reduce uncertainties. Provide the How-To Procedures for future sites.